

### Amendments to the Specification:

Please replace paragraph [0006] with the following amended paragraph:

B' [0006] Among the semiconductor materials systems that have been investigated for a suitable 1.05 eV cell layer is GaInNAs. The interest in this system was sparked initially by the surprising observation by Weyers *et al*, *Jpn. J. Appl. Physics* 31 (1992) pp. L853, that the dilute alloy GaAs<sub>1-x</sub>N<sub>x</sub> has a giant conduction band bowing, Neugebauer, *et al*, *Phys. Rev. B.* 51 (1995) pp. 10568, and then by the demonstration by Kondow *[[et al.]] et al.*, in 1996 that the quaternary alloy Ga<sub>0.92</sub>In<sub>0.08</sub>N<sub>0.03</sub>As<sub>0.97</sub> could be grown lattice matched to GaAs with a bandgap of 1.0 eV *J. Cryst. Growth* 164 (1996) pp. 175. The 8% In was used by Kondow *et al.*, along with the Ga, As, and N, to achieve lattice matching with a GaAs substrate. However, the photoluminescence of Ga<sub>0.92</sub>In<sub>0.08</sub>N<sub>0.03</sub>As<sub>0.97</sub> is poor. In spite of dilute GaAs<sub>1-x</sub>N<sub>x</sub> having the desired 1.0 eV bandgap and the ability to lattice match it to GaAs by the addition of In to the alloy, the very poor electron mobilities in such dilute GaAs<sub>1-x</sub>N<sub>x</sub> based alloys has inhibited any further significant progress toward using such an alloy in a photoelectric device, such as a monolithic, quadruple junction, solar cell.

Please replace paragraph [0031] with the following amended paragraph:

B2 [0031] An example high efficiency, monolithic, quadruple junction, solar cell 10 constructed according to the principles and by a method of this invention is shown diagrammatically in Figure 1. An active, light-absorbing cell 12 comprising a dilute alloy of [[GaAs<sub>1-x-y</sub>N<sub>x</sub>Bi<sub>y</sub>]] GaAs<sub>1-x-y</sub>N<sub>x</sub>Bi<sub>y</sub> (sometimes abbreviated as GaAs:N:Bi) with a bandgap of about 1.05 eV is positioned between a Ge cell 11 (bandgap of 0.67 eV) and a GaAs cell 13 (bandgap of 1.42 eV) in the monolithic, quadruple junction, solar cell 10, which also has a InGaP cell 14 (bandgap of 1.90 eV) overlaying the GaAs cell 13 and a Ge substrate 15, which is doped to provide a n-p

B2  
junction 21 as the bottom Ge cell 11. Of course, the solar cell 10 also has a conventional bottom contact layer 16 and top grid 17 to facilitate electrical connection of the cell 10 into a circuit (not shown). Other conventional features, such as anti-reflective (A.R.) coating 19, window layer 25 (to passivate the surface), contact layer 18 (to facilitate ohmic contacts), and back surface reflectors (BSR) 26, 27, 28, 29, 30, are also shown, although these components are well-known in the art and are not part of this invention. The BSR layers 26, 27, 28, 29, 30 are designed to be lattice matched to, but with higher bandgaps than, the regions they surround.

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Please replace paragraph [0032] with the following amended paragraph:

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B3  
[0032] When solar radiation 30 irradiates the solar cell 10, the higher energy, shorter wavelength portion of the solar spectrum (e.g., wave-lengths in a range of about 652  $[[\boxed{\text{m}}]]\text{nm}$  and below) is absorbed and converted to electric energy substantially in the top (fourth) cell 14 of InGaP, while the lower energy, longer wavelength solar radiation is transmitted into the next (third) cell 13 of GaAs. The next to highest energy range of solar radiation (wavelength of about 873  $[[\boxed{\text{m}}]]\text{nm}$  to 652  $[[\boxed{\text{m}}]]\text{nm}$ ) is then absorbed and converted to electric energy substantially in the GaAs third cell 13, which also transmits lower energy solar radiation to the second cell 12 of GaAs:N:Bi. This GaAs:N:Bi second cell 12 is fabricated according to this invention, as will be explained in more detail below. Solar radiation in the range of about 1180  $[[\boxed{\text{m}}]]\text{nm}$  to 873  $[[\boxed{\text{m}}]]\text{nm}$  is absorbed and converted to electric energy substantially in this second cell 12, while the remaining unabsorbed, lower energy radiation is transmitted to the first or bottom cell 11 of Ge. The bottom cell 11 absorbs and converts solar radiation in a range of about 1850  $[[\boxed{\text{m}}]]\text{nm}$  to 1180  $[[\boxed{\text{m}}]]\text{nm}$  to electric energy. Therefore, a monolithic, quadruple junction, solar cell 10 constructed as described above can absorb and convert enough of the solar radiation spectrum to electric energy to approach an overall cell efficiency of 40% AM1.

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Please replace paragraph [0037] with the following amended paragraph:

BY [0037] The GaAs:N:Bi alloy used for the second cell 12 is fabricated by isoelectronic co-doping the GaAs alloy with both nitrogen (N) and bismuth (Bi), preferably simultaneously. While the giant conduction band bowing observed by Weyers ~~et al~~ et al., in  $\text{GaAs}_{1-x}\text{N}_x$  appeared to demonstrate that the addition of N to GaAs can reduce the bandgap of GaAs significantly, and while the subsequent fabrication of the  ~~$\text{Ga}_{0.92}\text{In}_{0.08}\text{N}_{0.03}\text{As}_{0.97}$~~   $\text{Ga}_{0.92}\text{In}_{0.08}\text{N}_{0.03}\text{As}_{0.97}$  alloy by Kondow *et al.*, utilized that concept to fabricate a semiconductor material with the desired 1.0 eV bandgap, a significant part of this invention and the motivation for the solutions, processes, and devices described herein is the realization of the following: (i) that, unfortunately, the N in the alloy also creates isoelectronic traps, which have defeated all attempts to utilize such giant bowing of the conduction band; and (ii) that the N in the GaAs does not just induce the bowing of the conduction band of GaAs, but, instead, the N impurities participate directly in the formation of the conduction band via the formation of a deep acceptor N impurity band. A further significant part of this invention includes the discoveries that: (i) Isoelectronic co-doping of GaAs with both N and Bi simultaneously also creates a deep donor; and (ii) The effect of such deep donors on the valence band mirrors the effect of N on the conduction band and virtually eliminates the adverse effects of the N-based isoelectronic traps that have previously defeated use of the otherwise beneficial effects (e.g., bandgap reduction) of N in GaAs semiconductor materials used as photocells. Specifically, such isoelectronic co-doping of GaAs with both N and Bi virtually eliminates the very poor electron mobilities and hopping-like transport characteristics, which are inherent in GaAs that is doped only with N, and it counteracts the increased Madelung energy effects of N in the GaAs crystal lattice that limit solubility of the N

B4 in the GaAs material. Such co-doping with N and Bi is isoelectronic, because both N and Bi are in the same group on the periodic table of the elements as the host elements they replace.

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Please replace paragraph [0041] with the following amended paragraph:

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B5 [0041] Conventional wisdom would imply that isoelectronic substituents, such as N in GaAs, should result in the formation of an alloy, because N and As are isoelectronic, i.e., both are group V elements on the periodic table of the elements, and that N should not create a defect level in GaAs. However, recent experiments by Zhang *et al.*, *et al.*, *Phys. Rev. B* 63, 85205 (2001) have (2001) have revealed that  $\text{GaAs}_{1-x}\text{N}_x$  is not really an alloy; it is instead a heavily doped semiconductor. N is a group V element that is strongly electronegative—much more so than the group V element As, which results in a N dopant having a short range impurity potential, i.e., behaving as an isoelectronic trap, that captures an electron, thereby leaving a hole bound to the long range coulomb potential in an acceptor-like wavefunction. In other words, such acceptor-like capture of an electron by the N impurities results in a long-range screened coulomb potential, which attracts a hole and results in a neutral excited state, i.e., an exciton bound to an isoelectronic trap. Thus, the N in the GaAs behaves as an isoelectronic deep acceptor analogous to a charged acceptor in charge-doped semiconductors, i.e., semiconductors doped with atoms that substitute in the host from a different group on the periodic table of the elements.

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Please replace paragraph [0043] with the following amended paragraph:

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B6 [0043] For isoelectronic doping with N in GaAs, a higher concentration of N is beneficial in that it leads to the formation of an impurity band, as will be explained below, that merges with the GaAs conduction band, which is the origin of the apparent giant bowing of the conduction band in  $\text{GaAs}_{1-x}\text{N}_x$  observed by Weyers *et al.* Zhang *et al.*, *Phys. Rev. B* 63, 85205 (2001)

64 showed that high N doping levels ( $>10^{19} \text{ cm}^{-3}$  or 0.1%) lead to such impurity bands that merge with the GaAs conduction band. However, since N behaves like a deep acceptor, such higher concentrations of N in  $\text{GaAs}_{1-x}\text{N}_x$ , i.e., about 0.1% or greater, cause carrier transport problems in the  $\text{GaAs}_{1-x}\text{N}_x$  alloy in much the same way that normal charged dopants at concentrations of about 0.1% or higher interfere with carrier transport properties in conventional, charge doped semiconductor materials. It is evident, therefore, that it is not possible to make a decent solar cell with GaAs:N and that attempts to do so will be futile. Further, even though higher concentrations of N would enhance the apparent giant bowing of the conduction band in  $\text{GaAs}_{1-x}\text{N}_x$ , the solubility of N in GaAs has been limited to about at 3%. It is noted that content and concentrations of isoelectronic dopants in descriptions of inventions herein are expressed in terms of atomic percent (at. %) of the anion sublattice of a crystal lattice, rather than for the entire crystal lattice, since it is assumed that all but a negligibly small number of the isoelectronic dopants fall on anion sites in the crystal lattice. While it is possible that a very small number of the isoelectronic dopants may fall on cation sites or interstitially, [[but]] such small number is negligible.

Please replace paragraph [0044] with the following amended paragraph:

67 [0044] Several efforts to incorporate higher concentrations of N in GaAs:N, such as by growing  $\text{GaAs}_{1-x}\text{N}_x$  out of thermodynamic equilibrium (Miyamoto *et al.*, *et al.*, *J. Cryst. Growth* 197 (1999) 67), have only further exacerbated problems with electron mobilities. This solubility limit is due to the strong electronegativity and the small size of N atoms, which, when substituted for As atoms in the host lattice, result in an increase of Madelung energy. When more N is forced into the  $\text{GaAs}_{1-x}\text{N}_x$ , it causes distortions in the lattice structure. Addition of In to compensate for such lattice structure distortions, as has been tried by

B7 S.R. Kurtz ~~et al.~~, et al., *Appl. Phys. Lett.* 77 (2000) 400, does not solve the problem of poor carrier mobilities.

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Please replace paragraph [0046] with the following amended paragraph:

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B8 [0046] To explain further, reference is made to Figures 2, 3, and 4, wherein Figures 2 and 3 illustrate dopant energy levels of conventional charged dopant acceptors and donors in a semiconductor material. In Figure 2, the conduction band energy  $E_c$  and valence band energy  $E_v$  are illustrated for a semiconductor material with a direct bandgap, i.e., wherein the minimum  $E_c$  and the maximum  $E_v$  both occur where the momentum vector  $[[k = 0]]$   $k = 0$ . In other words, an electron crossing the bandgap 40 has only to change its energy, but not its momentum, as opposed to an indirect bandgap material in which such an electron crossing the bandgap would also have to change its momentum. A conventional p-type charged dopant is an acceptor type atom, which is usually of one group to the left of a host element on the periodic table of the elements, i.e., one fewer electron in the outer energy shell. Such a conventional, charged acceptor dopant band 42 is illustrated in Figure 2, which shows that the conventional, charged acceptor dopant energy level is closer to the valence energy band  $E_v$  than to the conduction energy band  $E_c$ . A conventional, charged donor dopant band 44, as shown in Figure 3, is closer to the conduction energy band  $E_c$  than to the valence energy band  $E_v$ .

Please replace paragraph [0054] with the following amended paragraph:

[0054] However, when a large number of the isoelectronic dopant atoms are introduced into the host crystal lattice, i.e., more than about  $10\text{cm}^{-3}$ , the interaction between neighboring dopant atoms, i.e.,  $[[\text{"}]]$  pair interaction, triplet interaction, etc., in turn generates impurity bands. For heavy doping, such as is used for N (or Bi) in GaAs or in GaP, it is these various impurity levels generated by the impurity interactions that generate "bound states" whose energy levels merge

B8 with the conduction band (or valence band in the case of Bi), and such merger gets manifested as the bandgap bowing.

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Please replace paragraph [0058] with the following amended paragraph:

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B9 [0058] The impurity levels introduced by normally used charged acceptors, such as impurity level 42 illustrated in Figure 2, are located typically a few meV, [[i.e.]] e.g., about 20 meV, above the valence band edge  $E_v$ . Likewise, impurity levels introduced by normally used charged donors, such as impurity level 44 illustrated in Figure 3, are typically a few meV below the conductor band edge  $E_c$ . If the depth of these levels introduced by impurities were to be greater than the room temperature Boltzmann energy  $kT = 26$  meV, then most of the dopants would not be ionized at room temperature, thus would not behave as acceptors or donors. Impurity levels induced by charged acceptors or donors that are much deeper than 26 meV are referred to as deep levels.

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Please replace paragraph [0061] with the following amended paragraph:

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B10 [0061] Referring again to Figure 1, Ge can be used for the bottom or first cell 11 in the monolithic, quadruple junction solar cell 10 to provide the desired 0.67 eV bandgap for the solar cell 10, because the isoelectronically co-doped GaAs:N:Bi alloy of this invention can be grown nearly lattice matched with Ge, i.e., within about 0.2% misfit strain, to provide sufficient durability and carrier mobility for an efficient solar cell device. While Ge has an indirect bandgap, it is still suitable for the bottom cell 11 when used as a substrate 15 that also incorporates the Ge bottom cell 11, because the substrate 15 provides sufficient thickness for the Ge cell 11 to absorb substantially all the light in the 1850 [[ $\mu$ m]]nm to 1180 [[ $\mu$ m]]nm wavelength range.

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Please replace paragraph [0062] with the following amended paragraph:

B11 [0062] Any known procedure for co-doping, which is well-known in the art, can be used to accomplish the isoelectronic co-doping of alloys according to this invention, such as sequential bombardment of GaAs with N and Bi to implant overlapping N and Bi dopant profiles in the GaAs or by using OMVPE (organo-metallic vapor phase epitaxy) growth techniques. A suitable organic source for Bi [-] ---trimethylbismuth [-] ---is available commercially, for example, from Rohm and Haas of North Andover, Massachusetts. Nitrogen can be obtained from dimethylhydrazine, as is also well-known to persons skilled in the art, which can be obtained from the same company. The co-doping can also be achieved using molecular beam epitaxy (MBE) growth, vapor phase epitaxy (VPE) growth, or Liquid Phase Epitaxy growth (LPE). Co-doping using ion-implantation techniques are described, for example in S.P. Witrow *et al.*, "Ion Beam Annealing of Si Co-Implanted with Ga and As", *Mat. Res. Soc. Symp. Proc.*, Vol. 57, pp. 143-148, 1990, which is a current definitive, state-of-the-art reference and authority on co-doping, as well as in several other articles published since 1990. Also, as mentioned above, this invention is not limited to isoelectronic co-doping of GaAs with N and Bi. For example, but not for limitation, InP, GaP, InGaAs, and ZnSe can also be isoelectronic co-doped with "deep" acceptors and "deep" donors with similar benefits as those described above for GaAs alloys.

Please replace paragraph [0064] with the following amended paragraph:

B12 [0064] Referring to Figure 5, a two-junction tandem solar cell 50 according to this invention has a Si substrate 52, which is doped to provide a n-p junction 55, as is well-known to persons skilled in the art, to function as the bottom cell 54 with a bandgap of 1.1 eV. It also has a top cell 58 of isoelectronic co-doped GaP:N:Bi alloy according to this invention, which has a bandgap of 1.75 eV. The GaP:N:Bi alloy is charge doped with an acceptor, such as Zn or Cd, and with a



B12 donor, such as S or Se, to form a n-p junction 59. A tunnel junction 56 of ~~n<sup>++</sup>-and-p<sup>++</sup>-doped~~ n<sup>++</sup>- and p<sup>++</sup>-doped Si is also provided between the bottom cell 54 and the top cell 58, as is within the capabilities of persons skilled in the art. Of course, the junctions 55, 59 could be inverted to [[p - n]] p-n junctions, and the ~~p<sup>++</sup>-n<sup>++</sup> p<sup>++</sup>-n<sup>++</sup>~~ tunnel junction 56 could be inverted to a ~~n<sup>++</sup>-p<sup>++</sup>~~ n<sup>++</sup>-p<sup>++</sup> tunnel junction, as would be within the capabilities of persons skilled in the art. Of course, a bottom contact 60 and grid contacts 62 are provided to connect the solar cell 50 into an electric circuit (not shown); as is also within the capabilities of persons skilled in the art. The back surface reflector (BSR) 63, anti-reflection coating (ARC) 49, window layer 61, and contact layer 63 are conventional and well-known to persons skilled in the art and not part of this invention.

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Please replace paragraph [0066] with the following amended paragraph:

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B13 [0066] To further exacerbate problems in using GaP on Si, GaP has a very slightly larger lattice than Si, and it has a thermal expansion coefficient that is about double that of Si. The best technology for growth of GaP on Si utilizes a two-step process in which a thin GaP layer is grown at low temperature to achieve 2-dimensional growth of polar GaP on non-polar Si substrates that are miscut to eliminate anti-phase boundaries associated with polar or non-polar growth, followed by high-temperature growth of GaP. Therefore, at the high-growth temperatures (~~>700°C~~ >700 °C) required for good quality MOCVD (metal-organic chemical vapor deposition) grown epilayers of GaP on Si, the misfit strain changes from 0.37% compressive at room temperature to about 0.65% compressive at the high growth temperature. This value of misfit strain at the growth temperature, which is .28% compressive greater than the room temperature misfit strain of 0.37% compressive, results in a typically [[1 μm]] 1 μm thick

B13 epilayer of GaP on silicon being mostly relaxed at the growth temperature. However, subsequent cool down to room temperature results in crystal cracking problems.

Please replace paragraph [0072] with the following amended paragraph:

B14 [0072] The example two-junction tandem solar cell 50 illustrated in Figure 5, utilized isoelectronic ~~[[do]]~~ co-doped GaP:N:Bi with a bandgap of about 1.75 eV (1.65 eV to 1.85 eV) according to this invention to fabricate the second or top cell 58 on the Si bottom cell 54 (fabricated on a Si substrate 52), which has a bandgap of about 1.1 eV. The top cell 58 absorbs light energy in a wavelength range of about 708 ~~[[μm]]~~nm and below and converts it to electricity, while the bottom cell 54 absorbs light energy in a wavelength range of about 1127 ~~[[μm]]~~nm to 708 ~~[[μm]]~~nm and converts it to electricity.

Please replace paragraph [0073] with the following amended paragraph:

B15 [0073] The example three-cell tandem solar cell 70 illustrated in Figure 6 has a Si first or bottom cell 74 fabricated on a Si substrate 72 with ~~[[n - p]]~~ n-p or ~~[[p - n]]~~ p-n doped active junction 75 and a bandgap of about 1.1 eV, similar to the bottom cell 54 in solar cell 50 described above. Also, a  $p^{++}-n^{++}$   $p^{++}-n^{++}$  or  $n^{++}-p^{++}$   $n^{++}-p^{++}$  Si tunnel junction 76 similar to the tunnel junction 56 in solar cell 50 is provided over the bottom cell 74. An isoelectronic co-doped GaP:N:Bi semiconductor alloy according to this invention with a bandgap of about 1.55 eV (1.45 eV to 1.65 eV) is utilized for the second cell 78. In general, the higher the concentration of the isoelectronic co-dopants, the lower the effective bandgap of the resulting isoelectronically co-doped semiconductor alloy. Therefore, once persons skilled in the art understand this invention, they will be able to tailor any of the semiconductor alloys discussed herein to the desired bandgaps. The GaP:N:Bi second cell 78 is charge doped to provide a ~~[[n - p]]~~ n-p or a ~~[[p - n]]~~ p-n junction 79, as described above for the second cell 58 of solar cell 50, a more

B15 heavily doped tunnel junction 80 is provided over the second cell 78 and a BSR layer 85, as will be understood by persons skilled in the art. A third or top cell 82 of isoelectronic co-doped GaP:N:Bi alloy with a bandgap of about 2.05 eV (1.95 eV to 2.15 eV) according to this invention is provided over the second cell 78, tunnel junction 80, and BSR layer 84. The GaP:N:Bi top cell is charged doped to form a  $[[n - p]]$  n-p or  $[[p - n]]$  p-n junction 83 similar to the doping for the junction 79 in the second cell 78, as will be understood by persons skilled in the art. A bottom contact 90 and top grid contacts 92 are also provided, as will be understood by persons skilled in the art.

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Please replace paragraph [0074] with the following amended paragraph:

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B16 [0074] The top cell 82 of the solar cell 70 absorbs light energy in a wavelength range of about 605  $[[\mu\text{m}]]$  nm and below and converts it to electricity, while the second cell 78 and bottom cell 75 absorb light energy in respective wavelength ranges of 605  $[[\mu\text{m}]]$  nm to  $[[200 \mu\text{m}]]$  800 nm and 800  $[[\mu\text{m}]]$  nm to 1127  $[[\mu\text{m}]]$  nm and convert it to electricity.

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Please replace paragraph [0078] with the following amended paragraph:

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B17 [0078] As shown in Figure 7, isoelectronic co-doping, according to this invention, can also be used to fabricate semiconductor diode edge-emitting lasers 120 on GaAs substrates, which operate in the 1.55 or 1.3  $\mu\text{m}$  wavelength regions for fiber-optic network communications. An n-type GaInP<sub>2</sub> cladding layer (low refractive index optical confining layer) 126 is grown lattice matched over an n-type GaAs substrate 124 followed by a bottom GaAs separate confinement heterostructure (SCH) layer 127. The active region 128 (see inset in Figure 7) comprises a set of multiple quantum wells (MQW) 135 of isoelectronically co-doped GaAs:N:Bi:In, where each well is surrounded by GaAs barriers 136. The amount of isoelectronic co-doping of the MQW's 135 and the MQW 135 well widths are chosen to yield ground state transition energies near 0.8—

~~0.93 eV~~ 0.8 ~ 0.93 eV (1.55 or 1.3  $\mu\text{m}$ ). The In is added to provide an additional parameter for lattice matching so that the N to Bi ratio can be adjusted independently for optimally regularizing the behavior of the alloy. The GaAs top SCH layer 129 is then grown followed by the top p-type GaInP<sub>2</sub> cladding layer 130 and a top contact stripe 132. The overall structure 120 is that of a p-i-n diode. When a voltage is applied to the top contact 132 and bottom contact 122 to forward bias the p-i-n diode, the barriers 136 in the MQW's 135 provide quantum confinement for the electrons and holes injected from the n (126) and p (130) regions, respectively, under the forward bias into the active region 128. The cladding layers 126 and 130 provide optical confinement for the radiation emitted as a result of the recombination of the injected electrons and holes in the MQW's 135. The thickness of the top and bottom separate confinement heterostructure (SCH) layers 127 and 129 is of the order of an optical wavelength, thereby confining in the transverse direction the optical Fabry-Perot cavity bounded longitudinally by the front and rear mirrors formed by the cleaved faces 133 and 131 respectively. The mirrors may be coated to increase or decrease their reflectivity as necessary or desired to produce and emit a laser light beam 134, as is understood by persons skilled in the art. Carrier flow in the vertical direction follows the contour defined by the lateral stripe shape of the top contact 132. Thus, the lasing area is limited in the lateral direction to the stripe region defined by the top contact 132 because of gain guiding. Details such as contact layers for low resistance contacts and buffer layers are not shown. The edge-emitting laser in Figure 7 illustrates the most basic edge-emitting laser configuration. Other means of defining the stripe geometry for limiting the lateral width of the lasing area can be used such as those employed for the ridge-waveguide laser configuration or by using index guiding as for the buried heterostructure (BH) laser configuration, or by forming mesa or inverse mesa geometry structures. Many techniques, such as the use of reverse biased diodes as lateral current

B17  
blocking layers, or oxide or polyimide insulating layers or deeply etched recesses for lateral isolation and lowering of parasitic capacitances, can be used as is within the capabilities of persons skilled in the art. Also, as is well within the capabilities of persons skilled in the art, by inserting a grating profile layer at the bottom or top interface of the cladding layers 130 or 126, a DFB (distributed feedback) laser or DBR (distributed Bragg reflector) laser can be realized, which has a very narrow frequency spectrum suitable for fiber-optic communications. Finally, any of the conventional growth techniques, such as MBE, MOCVD, VPE, or LPE (liquid phase epitaxy), can be used for the growth of the device, and the charged doping for  $[[n]]$  n-type and  $[[p\ type]]$  p-type layers, which is achieved by conventional techniques, can be interchanged.

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Please replace paragraph [0084] with the following amended paragraph:

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B18  
[0084] Isoelectronically co-doped GaAs, according to this invention, can also be used to fabricate VCSEL's (Vertical Cavity Surface Emitting Lasers) 180 to operate in the ~~1.55  $\mu$ m or~~ 1.3  $\mu$ m 1.55  $\mu$ m or 1.3  $\mu$ m wavelength regions, as shown in Figure. 8. A DBR (distributed Bragg reflector) stack 187 comprising n-type GaAs/ $Al_xGa_{1-x}As$  alternating layers is grown over an n-type GaAs substrate 188. The topmost layer 186 of the stack is made Al-rich. Next the bottom SCH layer 191 is grown using GaAs. This bottom SCH layer 191 is followed by growth of the active layer 185 (see inset) which comprises a set of multiple quantum wells (MQW) 193 of isoelectronically co-doped GaAs:N:Bi:In, where each well 193 is surrounded by GaAs barriers 194. The amount of isoelectronic co-doping of the MQW's 193 and the MQW 193 well widths are chosen to yield ground state transition energies near ~~0.8  $\sim$  0.93 eV~~ 0.8  $\sim$  0.93 eV (1.55 or 1.3  $\mu$ m). The top SCH layer 190 is next grown using GaAs followed by a DBR stack 183 comprising p-type GaAs/ $Al_xGa_{1-x}As$  alternating layers. The bottommost layer 184 of the DBR stack 183 is made Al-rich. A front metallic contact 182, and a back metallic contact 189

complete the growth. Any of the conventional methods that are well known to persons skilled in the art can be next used to expose the vertical cross-section of the device 180 to a steam environment at a temperature of  $[[400 - 450\text{ }^{\circ}\text{C}]]$   $400 \sim 450\text{ }^{\circ}\text{C}$  for a time designed to oxidize the Al-rich layers 184 and 186 in the DBR stacks 183 and 187 from the periphery, leaving a central, un-oxidized window region through which laser light 181 emanates. The resulting oxidized aperture layer 184, 186 serves as a current blocking layer (CBL). The p-type and n-type regions are obtained by charge doping of GaAs and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . The charged doping for the p-type and n-type regions are achieved by conventional techniques and of course the p-type and n-type regions can be interchanged. Other geometries for a VCSEL laser, which require other methods for generating the current blocking, which is the function of oxidized layers 184 and 186, can also be utilized as is within the capabilities of persons skilled in the art. Also, since utilizing two relatively low n-type DBR mirror stacks (instead of one p-type and one n-type as in Figure 8) reduces the free carrier absorption, which can be excessive at long wavelengths in p-type materials, this can be achieved by introducing a tunnel junction into the high index GaAs layer nearest to the optical cavity 185 in the top output mirror 183. Finally any of the conventional growth techniques, such as MBE or MOCVD, can be used for the growth of the device. Prior to this invention, only VCSEL lasers operating around the 800 nm near-infrared wavelength range were commercially available, because it is very difficult to fabricate the 1.55  $\mu\text{m}$  and 1.3  $\mu\text{m}$  wavelength devices. This limitation is due to the fact that these devices are generally based on the quaternary InGaAsP alloy system that could only be grown lattice matched to InP substrates, and it is very difficult to grow decent DBR stacks using this quaternary alloy. Thus, the InGaAsP based 1.55 and 1.3  $\mu\text{m}$  lasers are generally of the edge-emitting type instead of the VCSEL type. Since VCSEL lasers offer unique advantages over edge emitting lasers, and GaAs

618 technology is cheaper than InP technology, isoelectronic co-doping of GaAs according to this invention to fabricate the VCSEL 180 proves very advantageous. In addition, the isoelectronically co-doped laser 180 described above has the following advantages:

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Please replace paragraph [0089] with the following amended paragraph:

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619 [0089] Another application of isoelectronic co-doping semiconductor materials with deep acceptors and deep donors according to this invention is the ability to grow LED semiconductor devices on GaP or Si substrates. An example of such an application is a Red/NIR (near-infrared), i.e., 640-800 nm wavelength, High-Brightness LED 200 shown in Figure 9, which comprises an active region 202 of isoelectronically co-doped GaP, according to this invention, with a bandgap chosen to have a value in the range 1.55 - 1.93 eV to produce Red/NIR light. Isoelectronically co-doping GaP with deep acceptors such as N, and deep donors, such as Bi, can be used to lower the bandgap of GaP to a value in the range 1.55 - 1.93 eV to produce Red/NIR light whilst regularizing the properties of the alloy (enhancement of carrier mobilities, photoluminescence efficiency, carrier lifetime, and reduced tail states in the bandgap) according to this invention. Since this isoelectronically co-doped system (GaP:N:Bi), according to this invention, can be grown lattice matched to a GaP substrate, the Red/NIR LED 200 in the DH (double heterostructure) configuration 206, along with the n-GaP barrier layer 205, can be grown directly on the n-GaP substrate 204. The active region 202 can be a multiple quantum well (MQW) structure, as shown in Figure 9, or it can be a single isoelectronically co-doped GaP:N:Bi layer (not shown) for lower cost, albeit lower energy emission, LED devices, as will be understood by persons skilled in the art. The MQW active region 202 comprises multiple, alternating GaP barrier layers 203A and isoelectronically co-doped GaP:N:Bi well layers 203B. The quantum confinement provided by the MQW layers 203A, 203B serves to shift the LED emission toward

B19  
higher energies and, also, to lower the threshold current. The thick, transparent GaP substrate 204 serves as a thick ( $>200\ \mu\text{m}$ ) top window proving advantageous for simultaneous top and side extraction of light from the device. Moreover, after growth of the structure by MOCVD or MBE, the device can be transferred to a VPE growth system and a thick ( $\approx 50\ \mu\text{m}$ ) superstrate layer 208 of p-GaP can be grown over the p-GaP barrier layer 207. With a reflecting back contact 209, this structure enables all six cones of light (top, bottom and four side cones) from the device to be extracted. Surface texturing of the top and bottom surfaces can be employed to randomize the reflected light thus diminishing losses due to multiple light bounces through the active region. Details such as contact layers for low resistance contacts are not shown. The n-type and p-type regions are achieved by conventional charged doping and can be grown reversed. Finally, the geometrical shape of the device can easily be configured into the Truncated-Inverted Pyramid (TIP) geometry (as is well within the capabilities of persons skilled in the art) to allow for the maximum light extraction and thus for use in applications requiring High Brightness LED's in the ~~red/NIR~~ Red/NIR spectral region.

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Please replace paragraph [0090] with the following amended paragraph:

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B20  
[0090] As shown in Figure 10, isoelectronic co-doping according to this invention can also be used to grow ~~Red/NIR~~ Red/NIR, i.e.,  $[[640 - 800]]$  640-800 nm wavelength, LED's 210 monolithically on silicon. The isoelectronically co-doped system of the LED 200 described above and illustrated in Figure 9 can also be grown on a Si substrate 217, as shown in Figure 10, using a step-graded layer structure 216 to allow for accommodation of the 0.37% compressive mismatch strain between the GaP based DH configuration 219 and the Si substrate 217. As shown in Figure 10, a step-graded layer structure 216 is first grown over the silicon substrate 217 to accommodate the 0.37% compressive mismatch strain between the GaP based double



B20 heterostructure laser 219 with the Si substrate 217. This step-graded layer structure 216 comprises four layers of n-doped  $\text{GaP}_{1-x-y}\text{N}_x\text{Bi}_y$  grown consecutively over the Si substrate 217 with the composition of N and Bi for each layer adjusted such that the mismatch strain between adjacent layers is about 0.1% for the first three layers, and is about 0.07% between the third and fourth layer of the step graded layers 216. The thickness of the first three layers of the step graded layers 216 is roughly  $0.3\ \mu\text{m}$  and that of the fourth layer is  $0.8\ \mu\text{m}$ . This arrangement allows the final network of misfit dislocations arising from the last composition step-grade to evolve fully, leaving only a very low density of threading dislocations to propagate into the DH configuration layers 219. The active region 214 in this LED 210 can also be either a MQW structure, as shown in Figure 10, or it can be a single isoelectronically co-doped  $\text{GaP:N:Bi}$  layer (not shown) for lower cost, albeit lower energy emission, LED devices. An MQW structure for the active region 214 comprises multiple, alternating GaP barrier layers 221 and isoelectronically co-doped  $\text{GaP:N:Bi}$  well layers 222, which provide quantum confinement to shift LED emission toward higher energies and lower threshold current as compared to a single  $\text{GaP:N:Bi}$  layer active region. The p-GaP superstrate 212, the DH configuration layers 219, comprising either the single  $\text{GaP:N:Bi}$  layer active region 214 (not shown) or the MQW active region 214 comprising the multiple, alternating GaP barrier layers 221 and isoelectronically co-doped  $\text{GaP:N:Bi}$  well layers 222, as well as the p-GaP barrier layer 213 and the n-GaP barrier layer 215, can be grown in a manner that is analogous to the superstrate layer 208 and the DH layer 206 discussed for Figure 9. However, in contrast to the High Brightness LED 200 of Figure 9, since the Si substrate 217 of the LED 210 in Figure 10 is not transparent to the light produced in the active region 214, and, instead will absorb such light. Therefore, only the top and side cones of light emitted from the DH configuration 219 can be extracted. The unique advantage of the

LED 210, however, is that it can be grown monolithically on Si, thereby allowing for such devices to be integrated directly with electronic circuits that have been fabricated alongside monolithically. Such monolithic integration of photonics and electronics would be very suitable for applications, such as in integrated transceiver chips for fiber-optic communications and for microdisplays. Further, while it is not necessary to this invention, the disadvantage of light absorption by the Si substrate 217 can be mitigated, and the efficiency of the LED 210 can be enhanced, by forming a distributed Bragg reflector (DBR) 120 comprising multiple, alternating layers of AlP and GaP between the barrier layer 215 and the step-graded layers 216 to reflect light back through the DH structure 219 and superstrate 212 before it reaches the light-absorbing Si substrate 217. Therefore, such reflected light emanates from the front surface of the LED 210 to enhance the energy and brightness of the emitted light instead of being absorbed by the Si substrate 217 and lost as heat. Also, if the LED 210 is to be coupled to an optical fiber (not shown), then the front contact 211 can be moved from the center to the edges, a recess for the fiber (not shown) can be etched into the superstrate 212, and an oxide isolation layer (oxide layer with a central aperture, which could be realized by oxidization of an inserted AlP layer from the periphery) can be inserted between layers 215 and 216 to limit the emitting area of the laser to the area under the fiber.

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Please replace paragraph [0092] with the following amended paragraph:

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[0092] As shown in Figure 11, isoelectronic co-doping according to this invention can also be used to fabricate a semiconductor diode, edge-emitting laser 230 on a Si substrate, which operates in the visible/NIR wavelength regions, i.e., 640 - 800 nm wavelengths. Step-graded layers 235 can be grown over the Si substrate 236 analogously as was done for the LED device 210 in Figure 10, to accommodate the 0.37% compressive mismatch strain between the Si

B21  
substrate 236 and an n-type  $\text{Al}_x\text{Ga}_{1-x}\text{P}$  bottom cladding layer (low refractive index optical confining layer) 234 lattice matched to a bottom GaP separate confinement heterostructure (SCH) layer 243. The active region 242 (see inset in Figure 11) comprises a set of multiple quantum wells (MQW) 244 of isoelectronic co-doped  $\text{GaP:N:Bi:In}$  according to this invention, where each well 244 is surrounded by GaP barriers 245. The amount of isoelectronic co-doping of the MQW's 244 and the MQW 244 well widths are chosen to yield MQW 244 ground state transition energies near 1.55 - 1.93 eV (~~640-800 nm~~ 640-800 nm). The GaP top SCH layer 233 is then grown followed by the top p-type  $\text{Al}_x\text{Ga}_{1-x}\text{P}$  cladding layer 232, a GaP surface passivation layer 246, and a top contact stripe 231. The overall structure is that of a p-i-n diode. When a voltage is applied to the top contact 231 and bottom contact 237 to forward bias the p-i-n diode, the barriers 245 in the MQW's 244 provide quantum confinement for the electrons and holes injected from the n-type 234 and p-type 232 regions, respectively, under the forward bias into the MQW active region 242. The cladding layers 232 and 236 provide optical confinement for the radiation emitted as a result of the recombination of the injected electrons and holes in the MQW's 244. The thickness of the top and bottom separate confinement heterostructure (SCH) layers 233 and 243 is of the order of an optical wavelength, thereby confining in the transverse direction the optical Fabry-Perot cavity bounded longitudinally by the front and rear mirrors formed by the cleaved faces 240 and 241, respectively. The mirrors 240, 241 may be coated to increase or decrease their reflectivity to produce and emit a laser beam 239 from an edge of the MQW active layer 242. Carrier flow in the vertical direction follows the contour defined by the lateral stripe shape of the top contact 231. Thus, the lasing area is limited in the lateral direction to the stripe region defined by the top contact 231, because of gain guiding. Details such as

B21 contact layers for low resistance contacts and buffer layers are well-known to persons skilled in the art, thus are not shown here.

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Please replace paragraph [0093] with the following amended paragraph:

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B22 [0093] The edge-emitting laser 230 in Figure 11 illustrates the most basic edge-emitting laser configuration. The alloy composition of the SCH layers 233, 243 may be linearly, parabolically, or step graded as in GRINSCH (graded index separate confinement heterostructure) lasers (here one would use  $\text{Al}_x\text{Ga}_{1-x}\text{P}$  for the cladding layers 232, 234 and grade the composition of  $x$  from  $[[x=0]]$   $x=0$  to the value of  $x$  in the cladding layers 232, 234). Other techniques of defining the stripe geometry for limiting the lateral width of the lasing area can also be used, such as those employed for the ridge-waveguide laser configuration or by using index guiding as for the buried heterostructure (BH) laser configuration or by forming narrow mesas or inverse mesa geometry structures. Many techniques, such as the use of reverse biased diodes as lateral current blocking layers, or oxide or polymide insulating layers or deeply etched recesses for lateral isolation and lowering of parasitic capacitances, can be used as is within the capabilities of those familiar with the art. Also, as is well within the capabilities of those familiar with the art, by inserting a grating profile layer at the bottom or top interface of the cladding layers 232 or 234, a DFB (distributed feedback) laser or DBR (distributed Bragg reflector laser) can be realized which has a very narrow frequency spectrum suitable for fiber-optic communications. Finally, any of the conventional growth techniques, such as MBE or MOCVD or VPE or LPE, can be used for the growth of the device, and the charged doping for  $[[n]]$  n-type and p-type layers, which is achieved by conventional doping techniques, can be reversed.

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Please replace paragraph [0099] with the following amended paragraph:

823 [0099] Isoelectronic co-doping according to this invention can also be used advantageously in the area of Thermal Photovoltaics (TPV), where the source of radiant energy is blackbody radiation from a thermally heated source. The optimal bandgap of a TPV cell is 0.5 eV for absorption from a 1000K heat source. Prior to this invention, the best TPV cells were based on growing  $\text{In}_x\text{Ga}_{1-x}\text{As}$  on InP substrates with  $x$  chosen such that the bandgap of the  $\text{In}_x\text{Ga}_{1-x}\text{As}$  alloy was 0.5 eV. However, at this composition of  $[[x= 0.22]]$   $x = 0.22$ ,  $\text{In}_x\text{Ga}_{1-x}\text{As}$  is lattice mismatched to InP. Therefore, it has been necessary to resort to difficult growth procedures, such as growth of a sequence of step-graded layers in between the InP substrate and the TPV device active layer so as to distribute the mismatch strain by the consequent strain grading. However, that technique results in thicker and more complex structures. A thermal photovoltaic cell (TPV) 250 comprising an isoelectronic co-doped semiconductor material according to this invention is illustrated in Figure 12. This cell 250 circumvents the difficulties encountered in growing the  $\text{In}_x\text{Ga}_{1-x}\text{As}$  TPV cell mentioned above. The TPV cell 250 in this example comprises an isoelectronic co-doped InGaAs:N:Bi cell in a double heterostructure (DH) configuration 259 grown lattice matched to an  $n^+$  InP substrate 257. The active absorbing region comprises a p-n junction made up of p-type layer 254 of isoelectronically co-doped InGaAs:N:Bi and a n-type layer 255 of isoelectronic co-doped InGaAs:N:Bi, where the amount of co-doping is adjusted to lower the bandgap of InGaAs from the value 0.75 eV, for which it is lattice matched to InP, to a value 0.5 eV, whilst maintaining lattice matching to InP. The cell p-n junction active layer is sandwiched in the DH configuration 259 by  $p^+$  and  $n^+$  barrier layers 253, 256 of InGaAs at the composition for which this alloy is lattice matched to InP. The epilayer 253 serves as a widow/passivation layer and the epilayer 256 as a BSR layer. A  $p^+$  InGaAs layer 252 to

B23 facilitate low resistance contacts and metallic contact layers 251(a grid) and 258 complete the TPV cell device 250 structure. All the epitaxial layers 252-257 are grown lattice matched to the InP substrate 257. The growth can be accomplished using MBE, MOCVD, or VPE techniques, and the charged doping for n-type and p-type layers, which is achieved by conventional doping techniques, can be reversed. Also, since the InP substrate 257 is transparent (it has a bandgap of 1.34 eV) to radiation absorbed by the cells active region 254, 255, the top (grid) contact 251 and bottom contact 258 can be interchanged, i.e., the radiant heat energy 260 can be absorbed through the substrate 257 from below. Also, an additional InP:N:Bi isoelectronically co-doped bottom cell operating in tandem to the top cell 259 can be inserted monolithically between the top cell 259 and the substrate 257. Such additional bottom cell will have an active region p-n junction comprising p-type InP:N:Bi and n-type InP:N:Bi epilayers for which the amount of isoelectronic co-doping is adjusted to lower the bandgap of InP to a suitable value in the range 0.6 to 0.75 eV (for optimal tandem cell performance), whilst maintaining lattice matching to the InP substrate 258. Of course, a tunnel junction will have to be inserted between epilayer 256 and the InP:N:Bi cell. Also, the InP:N:Bi cell could be heavily isoelectronically co-doped to lower its bandgap to 0.5 eV and then the top  $\text{In}_x\text{Ga}_{1-x}\text{As}$  cell can be eliminated altogether, thus providing for a convenient single cell TPV device. Finally, although not shown in Figure 12, a plasma reflector layer which serves as a thermal mirror to reflect way radiant energy whose wavelength lies outside the spectral absorption region of the TPV cell active region (and to thus minimize heating effects) can be grown as the top layer of the cell.

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